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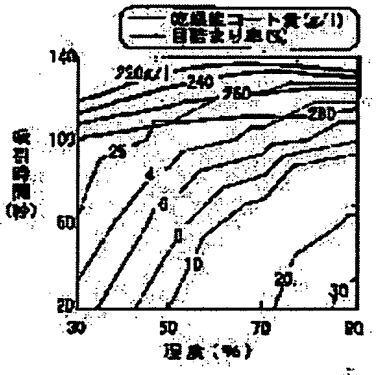
(54) METHOD FOR PRODUCING HONEYCOMB CATALYST

(57)Abstract:

PROBLEM TO BE SOLVED: To suppress clogging of cell passages when coating layers of a large coating weight are formed at a time by preventing flowage of slurry when excess slurry is removed.

SOLUTION: When the flow rate, temperature, relative humidity and passing time of air passing through cell passages are represented by V (m/sec), T (K), H (%) and t (sec), respectively, air is passed under conditions which satisfy both the formulae, $V \times t \geq -3{,}750+1{,}250 \times 1n(H)$ and $375-20 \times 1n(100-H) \leq T$. Since the degree of drying of slurry sticking to cell walls is made optimum, flowage due to air pressure is prevented.



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* NOTICES *

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CLAIMS

[Claim(s)]
[Claim 1] The drainage system slurry which uses oxide support powder as a principal component is made to adhere to the cell wall of the support base material of a honeycomb configuration with two or more cel paths. Dry the slurry which adhered to the cell wall while circulating air and removing the excessive slurry in this cel path, and it calcinates after that. The amount of coats is per volume of 1l. of this support base material. It is the manufacture approach of the honeycomb catalyst which forms a coat layer 240g or more. The manufacture approach of the honeycomb catalyst characterized by satisfying both following the (1) type and (2) types in the rate of flow of this air when V (m/second) and temperature are set to T (K) and H and (%) and circulation time amount are set to t (second) for relative humidity.
$Vxt \geq -3750+1250 \times \ln(H)$ .. (1)
$375-20 \times \ln(100-H) \leq T$ .. (2)
[Claim 2] Said relative humidity H is 70% or less and said temperature T. Said circulation time amount t is 273K or more and the manufacture approach of the honeycomb catalyst according to claim 1 which are 3 - 120 seconds.
[Claim 3] Said relative humidity H is the manufacture approach of the honeycomb catalyst according to claim 2 which is 40% or less.
[Claim 4] Said temperature T The manufacture approach of the honeycomb catalyst according to claim 2 which are 293K or more.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[Field of the Invention] This invention relates to the manufacture approach of the honeycomb catalyst which can form in homogeneity the coat layer which consists of oxide support powder in detail by the wash coat method about the manufacture approach of the honeycomb catalyst used for the catalyst for emission gas purification of an automobile etc.
[Description of the Prior Art] HC, CO, and NOx in [the purpose of reduction of environmental pollution in recent years to] exhaust gas etc. -- in order to remove harmful matter, various kinds of catalysts for emission gas purification are carried in the exhaust air system of an automobile. This catalyst for emission gas purification is made into the honeycomb configuration with many cel paths in order to raise a touch area with exhaust gas. In order to manufacture the catalyst for emission gas purification of such a honeycomb configuration, the support base material of a honeycomb configuration is first formed with shaping from heat-resistant ceramics, such as cordierite. Or the corrugated plate and plate which consist of a metallic foil are wound in the shape of a roll in piles, and the support base material of a honeycomb configuration is formed. And the slurry which made water distribute oxide support powder and binders, such as an alumina, is prepared, and after making it adhere to the cell wall of a support base material, a coat layer is formed by the wash coat method dried and calcinated. Noble-metals drug solutions, such as a nitrate, are infiltrated into a coat layer after that, it is dried and calcinated, and noble metals are supported. Moreover, the catalyst powder which made oxide support powder, such as alumina powder, support noble metals beforehand is prepared, and there is also the approach of slurring it and forming a coat layer. In order to carry out the wash coat of the slurry, the approach of circulating a slurry to a support base material and blowing off an excessive slurry is in use. However, by this approach, especially when the viscosity of a slurry is high, there is a problem that a cel path carries out blinding by the slurry. Then, after being immersed into a slurry and pulling up, spraying the compressed air from the opening end face of the cel path of a support base material, or drawing in with negative pressure from an opening end face, and removing an excessive slurry is performed. Moreover, in order to support noble metals, after infiltrating into a coat layer or oxide support powder the adsorption supporting method which a noble-metals drug solution is contacted to a coat layer or oxide support powder, and is supported by adsorption, or a noble-metals drug solution, the sinking-in supporting method which a solvent is evaporated and is supported is learned. However, in case an excessive slurry is removed behind a wash coat, in order that a slurry may flow the inside of a cel path with a wind pressure, the problem that dispersion arises is in the thickness of a coat layer. This problem is remarkable to form a coat layer thickly especially. For example, the catalyst for emission gas purification which formed the hydrocarbon adsorption layer which turns into a lower layer from zeolite powder etc., and formed the three way component catalyst layer which supported platinum to the alumina at the upper layer is known. According to this catalyst for emission gas purification, a hydrocarbon adsorption layer is adsorbed in the hydrocarbon in exhaust gas, after exhaust gas temperature rises and a three way component catalyst is activated, the hydrocarbon currently adsorbed secedes from a hydrocarbon adsorption layer, and oxidation purification is carried out with a three way component catalyst in the low-temperature region where three way component catalysts, such as the time of starting, have not reached activation temperature. Therefore, there is an advantage that the purification activity in the low-temperature regions at the time of starting etc. improves. Per forming [11.] a coat layer with

many [constitutionally] amounts of coats with such a catalyst for emission gas purification of the two-layer structure, for example, a support base material, To form a coat layer 240g or more may be desired. However, when many coat layers were formed in this way, and the wash coat of many slurries was carried out at once, and removing an excessive slurry, there was a problem that a slurry flows the inside of a cel path, the coat layer of the downstream became thick, a cel path became narrow, and a pressure loss increased with a wind pressure. Then, making viscosity of a slurry low and lessening the amount which adheres at once is performed. If it does in this way, the slurry volume which flows with a wind pressure also decreases, and a comparatively uniform coat layer can be formed. However, it is necessary to carry out for forming the coat layer of desired thickness in this case by repeating a wash coat and desiccation / baking process two or more times, and there is a problem that a man day becomes great in it.

[Problem(s) to be Solved by the Invention] This invention is made in view of such a situation, and it aims at controlling the blinding of the cel path at the time of forming a coat layer with many amounts of coats at once.

[Means for Solving the Problem] The description of the manufacture approach of the honeycomb catalyst of this invention which solves the above-mentioned technical problem The drainage system slurry which uses oxide support powder as a principal component is made to adhere to the cell wall of the support base material of a honeycomb configuration with two or more cel paths. Dry the slurry which adhered to the cell wall while circulating air and removing the excessive slurry in the cel path, and it calcinates after that. The amount of coats is per volume of 1l. of this support base material. It is the manufacture approach of the honeycomb catalyst which forms a coat layer 240g or more. It is characterized by satisfying both following the (1) type and (2) types in the rate of flow of air, when V (m/second) and temperature are set to T (K) and circulation time amount of H, and (%) and air is set to t (second) for relative humidity.

$Vxt>=-3750+1250x\ln(H)$ .. (1)

$375-20x\ln(100-H)<=T$ .. (2)

Relative humidity H is 70% or less and temperature T. As for 273K or more and the circulation time amount t, it is desirable that they are 3 - 120 seconds. Moreover, it is still more desirable that it is 40% or less, and relative humidity H is temperature T. It is still more desirable that they are 293K or more.

[Embodiment of the Invention] By the manufacture approach of the honeycomb catalyst of this invention, air is circulated in a cel path on the conditions with which it is satisfied of both the above-mentioned (1) formula and (2) types in the rate of flow when V (m/second) and temperature are set to T (K) and H and (%) and circulation time amount are set to t (second) for relative humidity. It becomes possible for the moisture content taken from the slurry which adhered to the cell wall by this to become the optimal, and to be able to make the rate of blinding of the cel path by flow of a slurry into 4% or less, and to form the coat layer of desired thickness on a wash coat once. In the above-mentioned (1) formula, when the value of Vxt is smaller than the value of $-3750+1250x\ln(H)$, since the air content which circulates compared with the moisture content which should be taken from a slurry decreases and a desiccation degree becomes late, a slurry will flow and the rate of blinding will exceed 4%. moreover, it sets at an above-mentioned (2) ceremony -- if the value of $375-20x\ln(100-H)$ becomes smaller than T, since the moisture content with which there are too many moisture contents in the circulating air, and they are taken from a slurry decreases and a desiccation degree becomes late, a slurry will flow and the rate of blinding will exceed 4%. The above-mentioned (1) formula and (2) types are the followings, and were made and drawn. The rate of blinding of a cel path when changing various each factors of V, T, H, and t first, and removing the excessive slurry in a cel path was measured, respectively. When two or more obtained data were analyzed, as a result of taking Vxt (circulation air content) along an axis of ordinate, taking H (air humidity) along an axis of abscissa and plotting the rate of blinding, it became clear that the logarithm of the rate of blinding can be approximated by the linear expression which made both factors the variable. And the formula (1) from which the rate of blinding becomes 4% or less was drawn. Moreover, since the force of taking moisture from the slurry adhering to a cell wall is proportional to the capacity by which moisture can enter into the circulating air, it is proportional to 100-H. And the amount of saturated steam of the circulating air is proportional to the logarithm of

absolute temperature mostly. (2) types from which the rate of blinding becomes 4% or less were drawn using this principle and the actually obtained above-mentioned data. Therefore, by considering as the conditions with which are satisfied of both the above-mentioned (1) formula and (2) types, the moisture content which the circulating air takes from the slurry in a cel path increases. Therefore, since it is controlled that dry the slurry adhering to a cell wall promptly, viscosity rises, and a slurry flows with a wind pressure, it can make the rate of blinding of a cel path 4% or less. This invention is not restricted to especially the component of a slurry, but can use the slurry which uses oxide support powder as a principal component, and makes water a dispersion medium. The simple substance or two or more sorts of multiple oxides which are chosen from aluminum 2O3, SiO2, ZrO2, TiO2 and CeO2, a zeolite, etc. as oxide support can be used. The catalyst metal may be beforehand supported by this oxide support powder. Moreover, it is also the same as usual that binder components, such as alumina sol, an aluminium nitrate, a silica sol, and a zirconia sol, are added. As for the viscosity of a slurry, it is desirable to consider as 5 - 500 mPa-s. If viscosity is lower than this range, the slurry volume which adheres to a cell wall at the time of a wash coat will decrease, and the effectiveness of this invention will not be acquired. Moreover, if viscosity becomes higher than this range, the slurry from which there is too much slurry volume which adheres to a cell wall at the time of a wash coat, and it is removed by the wind pressure will increase, and a man day with it will occur. [the bad yield and] [useless] In order to make a slurry adhere to the cell wall of the support base material of a honeycomb configuration, it can carry out by it being immersed and pulling up a support base material in a slurry, as usual. Or the end side of support may be dipped into a slurry, and it may draw in from an other end side, and may be filled up with a slurry in a cel path. Moreover, in order to circulate air and to remove an excessive slurry in a cel path, the compressed air may be supplied in a cel path from the end side of a support base material, and you may draw in with negative pressure from an other end side side. An excessive slurry is removed from a cel path by this, and the slurry of predetermined thickness adheres and remains in a cell wall. And the slurry adhering to a cell wall dries by circulating air further, viscosity rises, and a flow by the wind pressure is prevented. The rate of flow (V) of the circulating air has the desirable range of 1-30m/second. If it will become difficult to remove an excessive slurry if the rate of flow is smaller than this, and the rate of flow becomes large from this, it will be removed to a required slurry and the amount of coats will fall. Moreover, as for the relative humidity (H) of the circulating air, considering as 70% or less is desirable, and it is desirable that it is especially 40% or less. If relative humidity (H) exceeds 70%, in order that desiccation of a slurry may be extremely overdue, it becomes easy to flow by the wind pressure, and is easy to generate blinding. Furthermore, as for the temperature (T) of the circulating air, it is indispensable that it is more than the melting point of water, and it is desirable that it is more than 20 degree C (293K). And the circulation time amount (t) of air has the desirable range for 3 - 120 seconds. The slurry which should be removed if circulation time amount (t) is short remains in a cel path, and blinding arises. Moreover, if circulation time amount (t) is too long, it will be removed to a required slurry and the amount of coats will become low. You may calcinate, after calcinating as it is, supplying hot blast, after the slurry adhering to a cell wall dried to some extent, and making it dry further. Baking conditions It is about 5 - 120 minutes at 200 to 700 degree C. Thereby, a coat layer is formed. When a catalyst metal is not contained in a coat layer, a catalyst metal is supported next and it considers as a desired honeycomb catalyst. It can choose from base metal, such as noble metals, such as Pt, Rh, Pd, and Ir, or Co, Cr, Mo, Fe, as a catalyst metal, and can be supported as usual using drug solutions, such as the nitrate. Moreover, NOx, such as alkali metal and alkaline earth metal Occlusion material may be supported.

[Example] Hereafter, an example explains this invention concretely. The support base material of the honeycomb configuration which consists of cordierite was prepared. This support base material is a diameter. 100mm, die length Nothing and its volume are 1.18L about the approximate circle column configuration of 150mm. moreover, two or more cels -- respectively -- a cross-section square -- nothing and cel consistency 600 cels / in2 it is . On the other hand, it is alumina powder. The 100 weight sections, the alumina sol (aluminum 2O3 is 10 % of the weight) 100 weight section, and the distilled water 50 weight section were mixed, the ball mill distributed, and the slurry was prepared. The viscosity of a slurry is 200 mPa-s and the mean particle diameter of alumina powder is 5 micrometers. The above-mentioned support base material was set in the aspirator, the above-

mentioned slurry was slushed from the base material upper limit side, and it drew in from the base material lower limit side. At this time, suction removal of the excessive slurry in a cel path was carried out, and in the cel path, it adjusted so that air might circulate by the rate of flow of V= 15 m/s. and the ambient atmosphere by the side of an other end side -- constant temperature -- it considered as the air of constant humidity, and the temperature of air was fixed 25 degrees C (T= 298K), and the experiment which removes the excessive slurry in a cel path for two factors of the relative humidity (H) of air and suction time amount (t) as various levels was conducted. after that it dries at 250 degrees C for 1 hour -- it calcinated at 500 degree C for 1 hour, and the coat layer was formed, respectively. The weight of the obtained coat layer was measured, respectively and the amount of coats of per support base material 1L was computed. Moreover, although blinding was carried out among two or more cel paths, the number was counted, and the rate of blinding was computed. The obtained result is arranged and it is shown in drawing 1 . the relative humidity (H) of the air which suction time amount (t) is taken [air] along an axis of ordinate, and circulates an axis of abscissa in drawing 1 -- taking -- etc. -- coat [**** / blinding] **** is shown. The relative humidity (H) of air is suction time amount at 70% or more (t). If it does not lengthen with 100 seconds or more, it turns out that it is difficult to make the rate of blinding into 4% or less, and 40% or less, then suction time amount (t) also understand that the relative humidity (H) of air can consider as 4% or less for the rate of blinding in a short time for 80 or less seconds. and the thing for which suction time amount (t) is adjusted in 3 - 120 seconds according to relative humidity (H) -- the rate of blinding -- 4% or less -- it can carry out -- and -- It is clear that the amount's [220 or more g/L and] of coats it can do mostly. And when blinding ****, such as 4 etc.% or less, are approximated by the logarithmic function and the rate of blinding approximates an axis of ordinate by the air content which applied the rate of flow (V) to suction time amount (t), as for blinding ****, such as 4 etc.%, the rate of blinding is expressed as 15xt=-3750+1250xln(H). Therefore, as for blinding ****, such as 4 etc.% or less, the rate of blinding is expressed with 15xt>=-3750+1250xln(H). Again 375-20xln(100-H) <=T is also materialized. Therefore, by circulating air on the conditions with which are satisfied of both the aforementioned (1) formula and (2) types, the rate of blinding can be controlled to 4% or less, and it is the amount of coats. In 220 or more g/L and a pan They are 240 or more g/L.

[Effect of the Invention] That is, according to the manufacture approach of the honeycomb catalyst of this invention, the blinding of the cel path at the time of forming a coat layer with many amounts of coats at once can be controlled.

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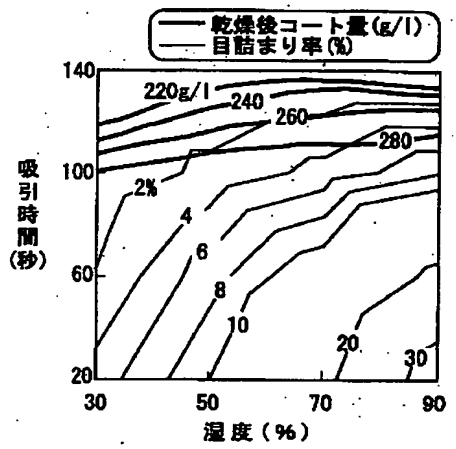
DRAWINGS

[Drawing 1]



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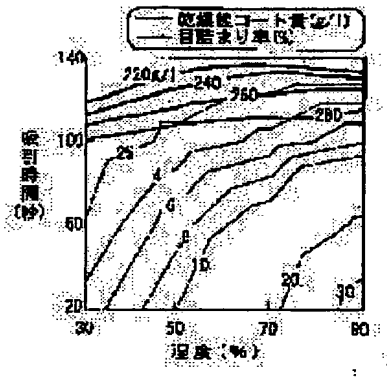
(54) METHOD FOR PRODUCING HONEYCOMB CATALYST

(57)Abstract:
PROBLEM TO BE SOLVED: To suppress clogging of cell passages when coating layers of a large coating weight are formed at a time by preventing flowage of slurry when excess slurry is removed.
SOLUTION: When the flow rate, temperature, relative humidity and passing time of air passing through cell passages are represented by V (m/sec), T (K), H (%) and t (sec), respectively, air is passed under conditions which satisfy both the formulae, $V \times t \geq -3,750+1,250 \times 1n(H)$ and $375-20 \times 1n(100-H) \leq T$. Since the degree of drying of slurry sticking to cell walls is made optimum, flowage due to air pressure is prevented.



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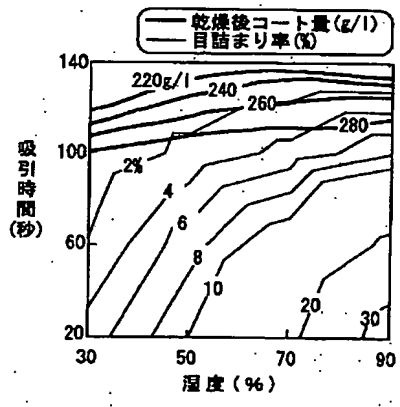
最終頁に続く

(54)【発明の名称】　ハニカム触媒の製造方法

(57)【要約】
【課題】余分なスラリーを除去する際のスラリーの流動を防止することで、コート量が多いコート層を一度に形成する際のセル通路の目詰まりを抑制する。
【解決手段】セル通路を流通する空気の、流速をＶ（ｍ／秒），温度をＴ（Ｋ），相対湿度をＨ（％），流通時間をｔ（秒）としたとき、下記（１）式及び（２）式の両方が満足される条件で空気を流通させる。
$V \times t \geq -3750+1250 \times \ln(H)$　・・（１）
$375-20 \times \ln(100-H) \leq T$　・・（２）
セル壁に付着したスラリーの乾燥度合いが最適となるため、風圧による流動が防止される。



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【特許請求の範囲】

【請求項１】　複数のセル通路をもつハニカム形状の担体基材のセル壁に酸化物担体粉末を主成分とする水系スラリーを付着させ、該セル通路内に空気を流通させて余分なスラリーを除去するとともにセル壁に付着したスラリーを乾燥しその後焼成して、コート量が該担体基材の体積１リットル当たり 240ｇ以上のコート層を形成するハニカム触媒の製造方法であって、該空気の、流速をＶ（ｍ／秒），温度をＴ（Ｋ），相対湿度をＨ（％），流通時間をｔ（秒）としたとき、下記（１）式及び（２）式の両方が満足されることを特徴とするハニカム触媒の製造方法。

$V \times t \geqq -3750+1250 \times \ln(H)$ ・・（１）

$375-20 \times \ln(100-H) \leqq T$ ・・（２）

【請求項２】　前記相対湿度Ｈは70％以下、前記温度Ｔは 273Ｋ以上、前記流通時間ｔは３～ 120秒である請求項１に記載のハニカム触媒の製造方法。

【請求項３】　前記相対湿度Ｈは40％以下である請求項２に記載のハニカム触媒の製造方法。

【請求項４】　前記温度Ｔは 293Ｋ以上である請求項２に記載のハニカム触媒の製造方法。

【発明の詳細な説明】

【発明の属する技術分野】本発明は、自動車の排ガス浄化用触媒などに用いられるハニカム触媒の製造方法に関し、詳しくは酸化物担体粉末からなるコート層をウォッシュコート法にて均一に形成できるハニカム触媒の製造方法に関する。

【従来の技術】近年の環境汚染の低減という目的から、排ガス中のHC，CO，NO_x などの有害物質を除去するために、自動車の排気系には各種の排ガス浄化用触媒が搭載されている。この排ガス浄化用触媒は、排ガスとの接触面積を高めるために、多数のセル通路をもつハニカム形状とされている。このようなハニカム形状の排ガス浄化用触媒を製造するには、先ずコージェライトなどの耐熱性セラミックスから成形によりハニカム形状の担体基材を形成する。あるいは金属箔からなる波板と平板を重ねてロール状に巻回してハニカム形状の担体基材を形成する。そしてアルミナなどの酸化物担体粉末とバインダを水に分散させたスラリーを調製し、担体基材のセル壁に付着させた後に乾燥し焼成するウォッシュコート法によりコート層を形成する。その後硝酸塩などの貴金属薬液をコート層に含浸させ、それを乾燥し焼成して貴金属を担持する。またアルミナ粉末などの酸化物担体粉末に予め貴金属を担持させた触媒粉末を調製し、それをスラリー化してコート層を形成する方法もある。スラリーをウォッシュコートするには、担体基材にスラリーを流通させ余分なスラリーを吹き払う方法が主流である。しかしこの方法では、スラリーの粘度が高い場合には特に、スラリーによってセル通路が目詰まりするという問題がある。そこでスラリー中に浸漬して引き上げた後に、担体

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基材のセル通路の開口端面から圧縮空気を吹き付けたり、開口端面から負圧で吸引したりして、余分なスラリーを除去することが行われている。また貴金属を担持するには、コート層又は酸化物担体粉末に貴金属薬液を接触させて吸着により担持する吸着担持法、あるいは貴金属薬液をコート層又は酸化物担体粉末に含浸させた後に溶媒を蒸発させて担持する含浸担持法などが知られている。ところがウォッシュコート後に余分なスラリーを除去する際に、風圧によってスラリーがセル通路内を流動するために、コート層の厚さにばらつきが生じるという問題がある。この問題は、コート層を特に厚く形成したい場合に著しい。例えば、下層にゼオライト粉末などからなる炭化水素吸着層を形成し、その上層にアルミナに白金を担持した三元触媒層を形成した排ガス浄化用触媒が知られている。この排ガス浄化用触媒によれば、始動時など三元触媒が活性化温度に到達していない低温域では、排ガス中の炭化水素が炭化水素吸着層に吸着され、吸着されていた炭化水素は排ガス温度が上昇して三元触媒が活性化された後に炭化水素吸着層から離脱して三元触媒によって酸化浄化される。したがって始動時などの低温域における浄化活性が向上するという利点がある。このような二層構造の排ガス浄化用触媒では、構成上コート量の多いコート層を形成すること、例えば担体基材１リットルあたり 240ｇ以上のコート層を形成することが望まれることがある。しかしながらこのように多くのコート層を形成する場合に、一度に多くのスラリーをウォッシュコートすると、余分なスラリーを除去する際に風圧によってスラリーがセル通路内を流動し、下流側のコート層が厚くなりセル通路が狭くなって圧損が増大するという問題があった。そこでスラリーの粘度を低くして、一度に付着する量を少なくすることが行われている。このようにすれば風圧によって流動するスラリー量も少なくなり、比較的均一なコート層を形成することができる。しかしこの場合には、所望の厚さのコート層を形成するにはウォッシュコートと乾燥・焼成工程を複数回繰り返して行う必要があり、工数が多大になるという問題がある。

【発明が解決しようとする課題】本発明はこのような事情に鑑みてなされたものであり、コート量が多いコート層を一度に形成する際のセル通路の目詰まりを抑制することを目的とする。

【課題を解決するための手段】上記課題を解決する本発明のハニカム触媒の製造方法の特徴は、複数のセル通路をもつハニカム形状の担体基材のセル壁に酸化物担体粉末を主成分とする水系スラリーを付着させ、セル通路内に空気を流通させて余分なスラリーを除去するとともにセル壁に付着したスラリーを乾燥しその後焼成して、コート量が該担体基材の体積１リットル当たり 240ｇ以上のコート層を形成するハニカム触媒の製造方法であって、空気の流速をＶ（ｍ／秒），温度をＴ（Ｋ），相対

湿度をＨ（％），空気の流通時間をｔ（秒）としたとき、下記（１）式及び（２）式の両方が満足されることを特徴とする。

Ｖ×ｔ≧－3750＋1250×ln（Ｈ）・・（１）

375－20×ln（ 100－Ｈ）≦Ｔ ・・（２）

相対湿度Ｈは70%以下、温度Ｔは 273K以上、流通時間ｔは３～ 120秒であることが好ましい。また相対湿度Ｈは40%以下であることがさらに望ましく、温度Ｔは 293K以上であることがさらに望ましい。

【発明の実施の形態】本発明のハニカム触媒の製造方法では、流速をＶ（ｍ／秒），温度をＴ（Ｋ），相対湿度をＨ（％），流通時間をｔ（秒）としたとき、上記（１）式及び（２）式の両方が満足される条件で、セル通路内に空気を流通させている。これによってセル壁に付着したスラリーから奪われる水分量が最適となり、スラリーの流動によるセル通路の目詰まり率を４％以下とすることができ、かつ一度のウォッシュコートで所望の厚さのコート層を形成することが可能となる。上記（１）式において、Ｖ×ｔの値が－3750＋1250×ln（Ｈ）の値より小さい場合には、スラリーから奪うべき水分量に比べて流通する空気量が少なくなり、乾燥度合いが遅くなるためにスラリーが流動して目詰まり率が４％を超えてしまう。また上記（２）式において、 375－20×ln（ 100－Ｈ）の値がＴより小さくなると、流通する空気中の水分量が多すぎてスラリーから奪われる水分量が少なくなり、乾燥度合いが遅くなるためにスラリーが流動して目詰まり率が４％を超えてしまう。上記（１）式及び（２）式は、以下のようにして導かれた。先ずＶ，Ｔ，Ｈ，ｔの各因子を種々変化させてセル通路内の余分なスラリーを除去したときの、セル通路の目詰まり率をそれぞれ測定した。得られた複数のデータを解析したところ、Ｖ×ｔ（流通空気量）を縦軸に取りＨ（空気湿度）を横軸に取って目詰まり率をプロットした結果、両因子を変数とした一次式で目詰まり率の対数を近似できることが明らかとなった。そして目詰まり率が４％以下になる式（１）を導いた。またセル壁に付着したスラリーから水分を奪う力は、流通する空気中に水分が入ることができる容量に比例するので、 100－Ｈに比例する。そして流通する空気の飽和水蒸気量は絶対温度の対数にほぼ比例する。この法則と実際に得られた上記データを用い、目詰まり率が４％以下になる（２）式を導いた。したがって上記（１）式と（２）式の両方が満足される条件とすることにより、流通する空気がセル通路内のスラリーから奪う水分量が多くなる。そのためセル壁に付着したスラリーは速やかに乾燥して粘度が上昇し、風圧によってスラリーが流動するのが抑制されるので、セル通路の目詰まり率を４％以下とすることができる。本発明はスラリーの成分には特に制限されず、酸化物担体粉末を主成分とし水を分散媒とするスラリーを用いることができる。酸化物担体としては、 Al_2O_3，SiO_2，ZrO_2，TiO_2，CeO_2，ゼオライトなどから選ばれる単体あるいは複数種の複合酸化物を用いることができる。この酸化物担体粉末には、予め触媒金属が担持されていてもよい。またアルミナゾル，硝酸アルミニウム，シリカゾル，ジルコニアゾルなどのバインダ成分が添加されることも従来と同様である。スラリーの粘度は５～500mPa・ｓとするのが好ましい。粘度がこの範囲より低いとウォッシュコート時にセル壁に付着するスラリー量が少なくなり、本発明の効果が得られない。また粘度がこの範囲より高くなると、ウォッシュコート時にセル壁に付着するスラリー量が多すぎて風圧で除去されるスラリーが多くなり、歩留まりが悪く無駄な工数が発生してしまう。ハニカム形状の担体基材のセル壁にスラリーを付着させるには、従来と同様にスラリー中に担体基材を浸漬して引き上げることで行うことができる。あるいは担体の一端面をスラリー中に浸し、他端面から吸引してセル通路内にスラリーを充填してもよい。またセル通路内に空気を流通させて余分なスラリーを除去するには、担体基材の一端面からセル通路内に圧縮空気を供給してもよいし、他端面側から負圧で吸引してもよい。これによりセル通路から余分なスラリーが除去され、セル壁には所定厚さのスラリーが付着して残る。そしてさらに空気を流通させることで、セル壁に付着したスラリーが乾燥して粘度が上昇し、風圧による流動が防止される。流通する空気の流速（Ｖ）は、１～30m／秒の範囲が好ましい。流速がこれより小さいと余分なスラリーを除去することが困難となり、流速がこれより大きくなると必要なスラリーまで除去されてしまいコート量が低下してしまう。また流通する空気の相対湿度（Ｈ）は70%以下とすることが好ましく、40%以下であることが特に望ましい。相対湿度（Ｈ）が70%を超えると、スラリーの乾燥が極端に遅れるため、風圧で流動しやすくなり目詰まりが発生しやすい。さらに、流通する空気の温度（Ｔ）は、水の融点以上であることが必須であり、20℃（ 293Ｋ）以上であることが望ましい。そして空気の流通時間（ｔ）は、３～ 120秒の範囲が好ましい。流通時間（ｔ）が短いと除去すべきスラリーがセル通路内に残留して目詰まりが生じる。また流通時間（ｔ）が長すぎると、必要なスラリーまで除去されてしまいコート量が低くなってしまう。セル壁に付着したスラリーがある程度乾燥した後は、そのまま焼成してもよいし、熱風を供給してさらに乾燥させた後に焼成してもよい。焼成条件は 200～ 700℃で５～ 120分程度である。これによりコート層が形成される。コート層に触媒金属が含まれない場合などには、この後に触媒金属が担持され、所望のハニカム触媒とされる。触媒金属としてはPt，Rh，Pd，Irなどの貴金属、あるいはCo，Cr，Mo，Feなどの卑金属から選択することができ、その硝酸塩などの薬液を用いて従来と同様に担持することができる。またアルカリ金属やアルカリ土類金属などのNO_x吸蔵材を担持してもよい。

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【実施例】以下、実施例により本発明を具体的に説明する。コージェライトからなるハニカム形状の担体基材を用意した。この担体基材は、直径 100mm、長さ 150mmの略円柱形状をなし、その体積は1.18Lである。また複数のセルはそれぞれ断面正方形をなし、セル密度は 600セル／in² である。一方、アルミナ粉末 100重量部、アルミナゾル（ Al_2O_3が10重量%） 100重量部、蒸留水50重量部を混合し、ボールミルで分散してスラリーを調製した。スラリーの粘度は200mPa・ｓであり、アルミナ粉末の平均粒径は５μｍである。上記担体基材を吸引装置にセットし、上記スラリーを基材上端面より流し込み、基材下端面より吸引した。この時セル通路内の余分なスラリーが吸引除去され、セル通路内には空気がＶ＝ 15m/sの流速で流通するように調整した。そして他端面側の雰囲気を恒温恒湿の空気とし、空気の温度は25℃（Ｔ＝ 298K）一定で、空気の相対湿度（Ｈ）及び吸引時間（ｔ）の２因子を種々の水準として、セル通路内の余分のスラリーを除去する実験を行った。その後 250℃で１時間乾燥し、 500℃で１時間焼成して、それぞれコート層を形成した。得られたコート層の重量をそれぞれ測定し、担体基材１Ｌあたりのコート量を算出した。また複数のセル通路のうち目詰まりしているものの数を数え、目詰まり率を算出した。得られた結果を整理して図１に示す。図１では、縦軸に吸引時間（ｔ）を取り、横軸に流通させる空気の相対湿度（Ｈ）を取って、等目詰まり率線と等コート量線を示している。空気の相対湿度　＊

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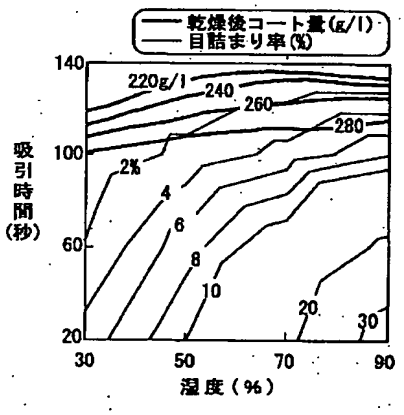
＊（Ｈ）が70%以上では、吸引時間（ｔ）を 100秒以上と長くしないと目詰まり率を４%以下とすることが困難であることがわかり、空気の相対湿度（Ｈ）を40%以下とすれば吸引時間（ｔ）が80秒以下の短時間で目詰まり率を４%以下とすることができることもわかる。そして相対湿度（Ｈ）に応じて吸引時間（ｔ）を３～120秒の間で調整することで、目詰まり率を４%以下とすることができ、かつ 220ｇ／Ｌ以上とコート量も多くできることが明らかである。そして目詰まり率が４%以下の等目詰まり率線は対数関数で近似され、縦軸を吸引時間（ｔ）に流速（Ｖ）をかけた空気量で近似すると、目詰まり率が４%の等目詰まり率線は$15\times t=-3750+1250\times \ln(H)$と表される。したがって目詰まり率が４%以下の等目詰まり率線は、$15\times t\geq -3750+1250\times \ln(H)$で表される。また $375-20\times \ln(100-H)\leq T$も成立する。したがって前記（１）式と（２）式の両方を満足する条件で空気を流通させることにより、目詰まり率を４%以下に抑制することができ、かつコート量を 220ｇ／Ｌ以上、さらには 240ｇ／Ｌ以上とすることができる。

【発明の効果】すなわち本発明のハニカム触媒の製造方法によれば、コート量が多いコート層を一度に形成する際のセル通路の目詰まりを抑制することができる。

【図面の簡単な説明】

【図１】流通空気の相対湿度と空気量を因子とした等目詰まり率線と等コート量線を示すグラフである。

【図１】



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